

UNIVERSITY OF FLORIDA
Integrated PV/Storage and PV/Storage/Lighting Systems

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Description: The goal is to increase the efficiency and reduce the cost of solar power through the integration of PV, Li-battery, and LED lighting technologies. Since all components are in the form of thin films, the PV/battery/LED system can be integrated as a single module. Since half of the materials cost of each device is the substrate, integrated module will also reduce materials costs and processing steps. Importantly, their integration further eliminates the need for inverters since they are all low-voltage devices. Such an integrated device can be used to store energy during the day and power the LED panel for lighting in the evening. In addition, we will explore the possibility of fabricating a semi-transparent module. The success of this Task will lead to a novel solar-power lighting panel that can be used as a sky light during the day and a lighting panel during the night without using grid-power. We not only will develop the technologies, but also integrate devices and perform technology-economic evaluation, including life-cycle costs.

Budget: \$576,000

Universities: UF

Progress Summary

There is great interest in developing renewable resources and improving the technologies for energy interconversions. The transformations of light into electricity (electrical energy generation in photovoltaic cells), electrical energy storage (rechargeable batteries) and electricity into light (light generation in light-emitting diodes) are three important interrelated areas that have attracted considerable research and commercial interest. Organic/polymer materials have been investigated for these transformations and undoubtedly play key roles in efficient production, transformation and utilization of solar energy. The main objective of the current work is to develop high efficiency solar energy at cheap cost for integrated PV/battery/lighting system. The development of self-contained power supplies that are suitable for electrical/lighting application depends upon the development of thin-film batteries and photovoltaic cells. In this project, we independently explore and develop the efficient and cost effective device component such as photovoltaic, batteries and organic light emitting devices.

In the PV area, our focus is to develop high efficiency polymer and hybrid PV cells. The highest power conversion efficiency of the solar cells developed under this project is 5.5%. In addition to fabricating solar cells on glass, we have developed the process to fabricate solar cells on plastic substrates. The highest efficiency obtained from all-plastic cells is 1.5%. In the battery area, we have started experimenting new synthesis methods that will lead to better surface stability of the electrode in the electrolyte. The preliminary rate testing data of the newly synthesized sample demonstrates the possibility of further improving the rate performance of the electrodes. In the OLED area, we have demonstrated a new method to fabricate large area, close-packed, hemispherical microlens array. Such transparent microlens array was further employed to enhance the light extraction efficiency of organic light-emitting devices by up to 70%.

2010 Annual Report

1. Broad band polymer solar cells (So)

Polymer solar cells (PSCs) are a promising alternative for low-cost renewable energy due to their potential to fabricate onto large area, light-weight flexible substrate and easy-processing fabrication

properties. To date, the polymer solar cells yielding the highest power conversion efficiencies are based on bulk-heterojunction (BHJ) structures whereby an interpenetrating network is formed between donor and acceptor components leading to increased interface area and enhanced exciton dissociation. However, the power conversion efficiency (PCE) of the polymer solar cell (PSC) achieved so far, not yet sufficient for large scale implementation. Morphology optimization of the active layer is one of the factors to improve the efficiency of PSCs. Besides the lateral phase separated morphology, the vertical phase segregation and grain size of the mixed molecules plays a crucial role in determining the exciton dissociation efficiency and charge extraction efficiency, and thus the overall power conversion efficiency. In order to maximize the device efficiency, the donor and acceptor molecules should segregate toward the anode and cathode, respectively. However, several donor polymer-PCBM systems have exhibited vertical phase segregation of polymer enrichment at the free (top) surfaces and abundance of fullerene derivatives at the organic/substrate (bottom) interfaces. So, a novel inverted device structure where the ITO acts as the cathode and the top metal contact is the anode was employed in order to accommodate the phase segregation. In this work, we have studied the effect of inverted device architecture with zinc oxide layer as bottom contact on the performance of low-bandgap donor-acceptor based polymer photovoltaic cell. The molecular structure of the poly ((4, 4- dioctyldithieno (3,2-b:2',3'-d) silole) -2,6- diyl-alt-(2,1,3-benzothiadiazole) -4,7-diyl) (DTS-BTD) and PC70BM is shown in Figure 1.

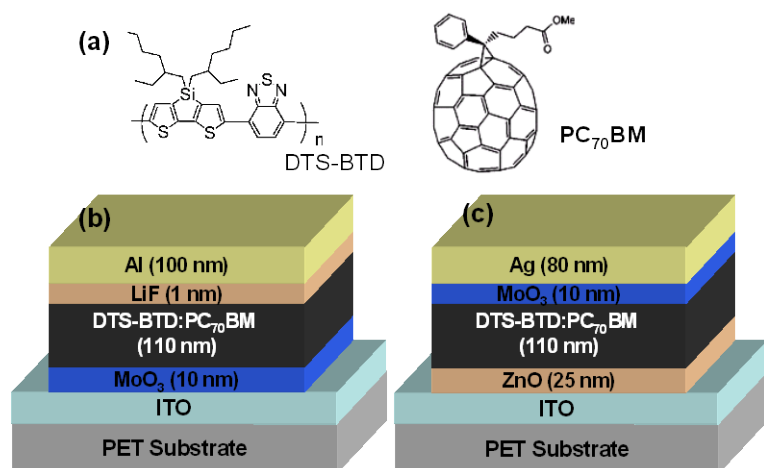


Figure 1. (a) Molecular structure of DTS-BTD and PC70BM, (b) schematic device structure of polymer solar cell with conventional and (c) inverted geometry.

Polymer cell	Device Geometry	JSC (mA/cm ²)	VOC (V)	FF (%)	PCE (%)
DTS-BTD:PC70BM	Conventional	12.71	0.61	61	4.91
	Inverted	16.48	0.59	56	5.51

Table 1 Photovoltaic characteristics of DTS-BTD/PC70BM solar cells.

As shown in Table 1, there is a substantial enhancement in short-circuit current due to the inverted structure, resulting in a power conversion efficiency of 5.5%.

2. Hybrid organic-inorganic solar cells and flexible solar cells (Xue)

We have studied hybrid solar cells based on conjugated polymers and colloidal CdSe nanocrystals. The CdSe nanocrystals were synthesized following literature reports, and after a ligand exchange with pyridine, these nanocrystals were mixed with a polymer P3HT in chlorobenzene or chloroform. We observed an abnormal aging behavior for the solution processed P3HT:CdSe solar cells, as the device performance is significantly improved after a 20-30 minutes of exposure to air without encapsulation. We further observed that the efficiency of such devices strongly depends on the size of the nanospheres as shown in Fig. 2. Such dependence is attributed to the amount of defects on the surface of CdSe nanocrystals, which act as recombination centers for photogenerated excitons and charges. The highest efficiency achieved for these P3HT:CdSe nanosphere solar cells is 1.9% under AM1.5G solar illumination.

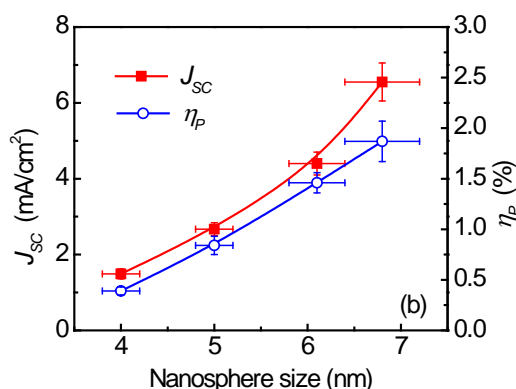


Fig. 2. Dependence of the short-circuit current and power conversion efficiency of hybrid P3HT:CdSe solar cells on the size of CdSe nanospheres.

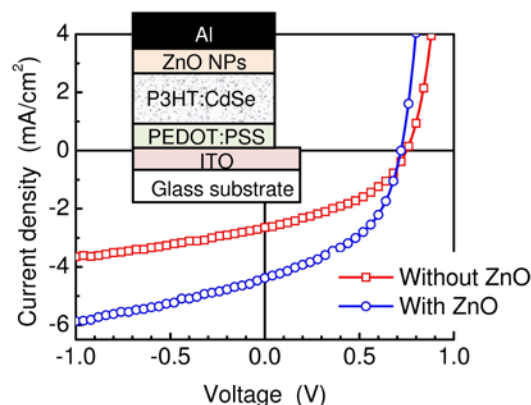


Fig. 3. Current density-voltage characteristics of hybrid P3HT:CdSe solar cells with or without a ZnO nanoparticle buffer layer. Inset shows the schematic device structure.

The efficiency of such devices was further enhanced by inserting a thin ZnO nanoparticle layer between the hybrid active layer and the Al cathode. As shown in Fig. 3, for 5 nm size CdSe nanospheres, the power conversion efficiency η_p was enhanced by approximately 70% after the incorporation of a 30 nm thick ZnO nanoparticle layer, which mostly comes from the enhancement in the short-circuit current density J_{sc} . The relative enhancement is reduced for cells with larger CdSe nanospheres. Nevertheless, a 30% increase in η_p was achieved for cells with 6-7 nm size CdSe nanospheres, leading to a maximum η_p of 2.5%. It is also important to note that the use of ZnO layer also dramatically increased the environmental stability of the devices.

P3HT has an absorption onset \sim 650 nm; hence the P3HT:CdSe hybrid solar cells do not harvest the abundant amount of infrared photons. We have also fabricated hybrid solar cells based on a low-gap polymer PCPDTBT, which has an absorption onset \sim 800 nm. A maximum η_p of 3.4% was achieved in such PCPDTBT:CdSe nanosphere based hybrid solar cells (with a ZnO nanoparticle layer), which is the highest reported efficiency for hybrid solar cells to date.

An important advantage of organic-based electronic materials is that they are compatible with flexible substrates and roll-to-roll manufacturing processes. Here we have successfully fabricated large-area polymer-based solar cells on plastic substrates. Using the normal structures (Fig. 4a) in which the ITO serves as the anode and a PEDOT:PSS layer coated on ITO serves as the hole injection layer, the solar cells exhibit poor fill factors. The fill factor of the solar cells was significantly improved when an inverted structure was used (see Fig. 4b), in which a ZnO nanoparticle layer was coated on the ITO serving as the cathode whereas a MoOx layer is inserted between the polymer active layer and a Al anode. A maximum

efficiency of ηP of 1.5% was achieved. Fig. 4c shows a picture of a flexible solar cell fabricated in the shape of a palm leaf.

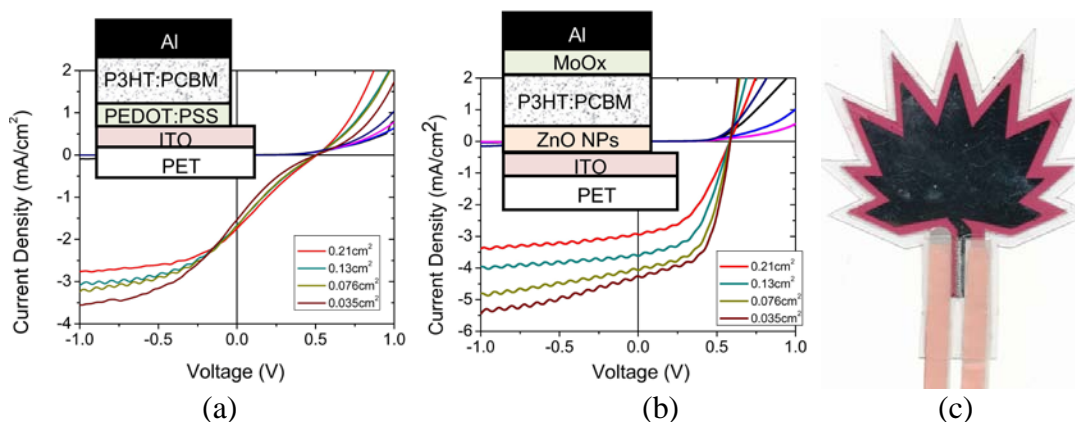


Fig. 4. Current density-voltage characteristics of polymer solar cells fabricated on PET substrates: (a) normal structures; (b) inverted structures; (c) a picture of a flexible solar cell fabricated in the shape of a palm leaf.

3. High Volumetric Energy Density and Long Life Lithium Batteries (Meng)

Over the past decades, while rechargeable batteries have made remarkable progress in terms of energy density, the improvement in energy density still falls short of the performance requirements for energy storage for renewable energy sources, such as solar, wind etc. for the Integrated PV/Battery Storage/Lighting system proposed in this FESC project, high volumetric energy density lithium ion batteries with long cycle life will be developed as a storage component in the solar-powered lighting module. To meet the grid-free operation requirements, conventional lithium ion batteries used in consumer electronics do not have the energy density and cycle life that will enable the lighting module to be completely grid-free..

New ultra high energy density and longer cycle life materials have been developed - a new class of electrodes based on Co-free, Ni and Mn containing Li transition metal oxides can be synthesized with inexpensive processes. We have optimized the synthesis conditions by understanding the critical role of stoichiometries of the precursors on the electrochemical properties of the proposed lithium excess manganese nickel oxide materials. We have investigated the change of crystal structure during electrochemical processes and its impact on cycling stability of the high energy lithium ion cells. The work has been published in C. R. Fell, K. J. Carroll, M. Chi, and Y. S. Meng, "Synthesis-Structure-Property Relations in Layered, "Li-excess" Oxides Electrode Materials $\text{Li}[\text{Li}_{1/3-2x/3}\text{Ni}_x\text{Mn}_{2/3-x/3}]\text{O}_2$ ($x=1/3, 1/4, \text{ and } 1/5$)", *Journal of the Electrochemical Society*, 157 (11), A1202, 2010.

The results obtained from XRD refinement, XPS, SEM, TEM and electrochemical testing show that the electrochemical properties of $\text{Li}[\text{Ni}_x\text{Li}_{1/3-2x/3}\text{Mn}_{2/3-x/3}]\text{O}_2$ are significantly influenced by synthesis conditions, particularly the amount of LiOH in the precursor. During the co-precipitation, an excess amount of LiOH:H₂O solution was used to ensure complete precipitation of the transition metal (TM) double hydroxide, $(\text{Ni}_x\text{Mn}_{2/3-x/3})(\text{OH}_2)$. In principle, all excess LiOH will be washed away with deionized water as shown in the experimental section. Nevertheless, several major differences are observed compared to the stoichiometric samples. Our high-resolution TEM and XPS studies reveal that the difference lies in the surface layer characteristics that are most probably caused by the presence of excess LiOH during co-precipitation. The excess LiOH might have led to the formation of a Nickel-rich compound with increased Ni³⁺ concentration at the surface of the particles due to the increased alkalinity

in the precipitating solution. Subsequent washing and high temperature synthesis cannot completely remove the surface layer, which resulted in larger polarization and more irreversible first cycle capacity due to side reaction with the electrolyte. It has been shown by previous work that intentional surface modifications of $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ($M=\text{Mn}$, Ni and/or Co) can significantly improve the electrochemical performance compared to bare-surface materials. The stoichiometric materials had well defined clean crystalline surfaces as shown in Figure 5a, while the LiOH excess materials showed different surface characteristics from the bulk, see Figure 5b.

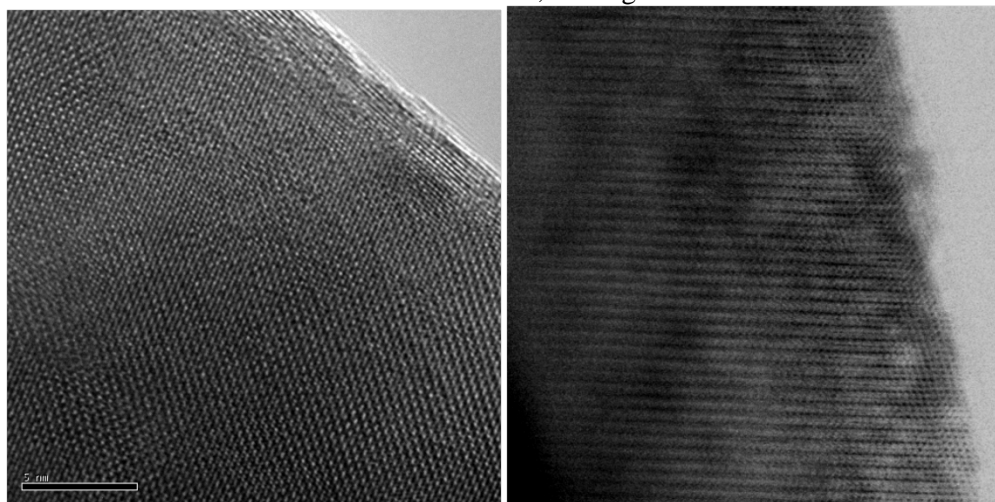


Fig. 5. TEM images of a) stoichiometric b) LiOH excess $\text{Li}[\text{Ni}_{1/5}\text{Li}_{1/5}\text{Mn}_{3/5}]\text{O}_2$ synthesized at 1000°C with furnace cooling.

Based on our results, it is optimal to synthesize the $\text{Li}[\text{Ni}_x\text{Li}_{1/3-2x/3}\text{Mn}_{2/3-x/3}]\text{O}_2$ material with a stoichiometric amount of LiOH precursor during the co-precipitation step, fire at 1000°C and allow the sample to furnace cool. The electrochemical performance of the material sintered at 1000°C shows consistently better reversible capacity compared to that synthesized at 900°C . Samples sintered at 1000°C show increased c and a lattice parameters, and less Li/Ni interlayer mixing. The lattice expansion and improved cation ordering may improve Li mobility leading to the improved electrochemical performance.

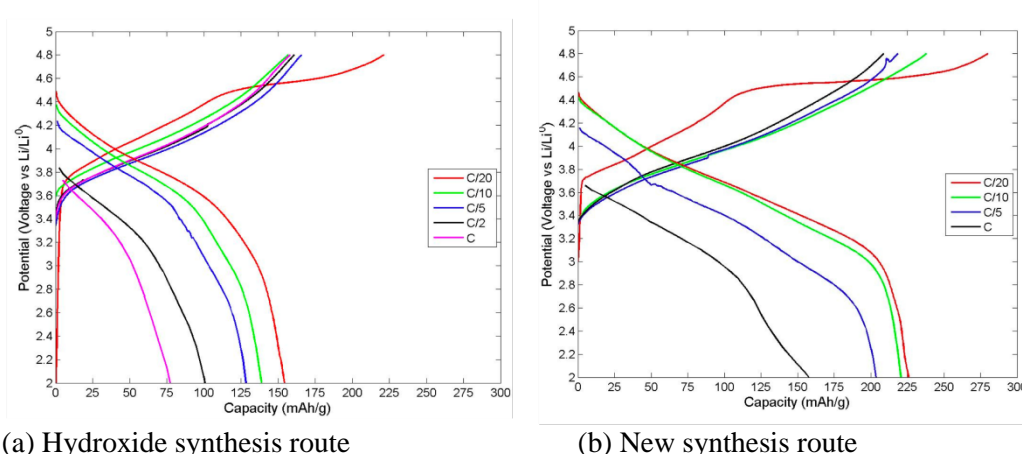


Fig. 6. Rate performance comparison of samples made by different synthesis processes.

We have also achieved significant progress in improving the rate capability of the materials. Since the surface has been identified as the major limiting factor, we have started experimenting new synthesis methods that will lead to better surface stability of the electrode in the electrolyte. The preliminary rate

testing data of the newly synthesized sample (shown in Fig. 6 above) demonstrates the possibility of further improving the rate performance of the electrodes. Research activities for the next reporting period will continue to focus on improving the rate capability and cycling ability of the new cathode materials in lithium ion cells.

4. Fabrication of large-area microlens array for enhancing the light extraction in OLEDs

One of the remaining challenges in the research on organic light-emitting devices (OLEDs) is to improve the light extraction efficiency from these devices, which is around 20% for flat-type devices due to total internal reflections. We have developed a method to easily fabricate a large-area hemispherical lens array. The fabrication process for the microlens array is illustrated in Fig. 7a, while images of the fabricated microlens array are shown in Fig. 7b. When such a close-packed, hemispherical microlens array was applied to the light emitting surface of an OLED, we obtained an up to 70% enhancement in the light extraction efficiency, as shown in Fig. 7c.

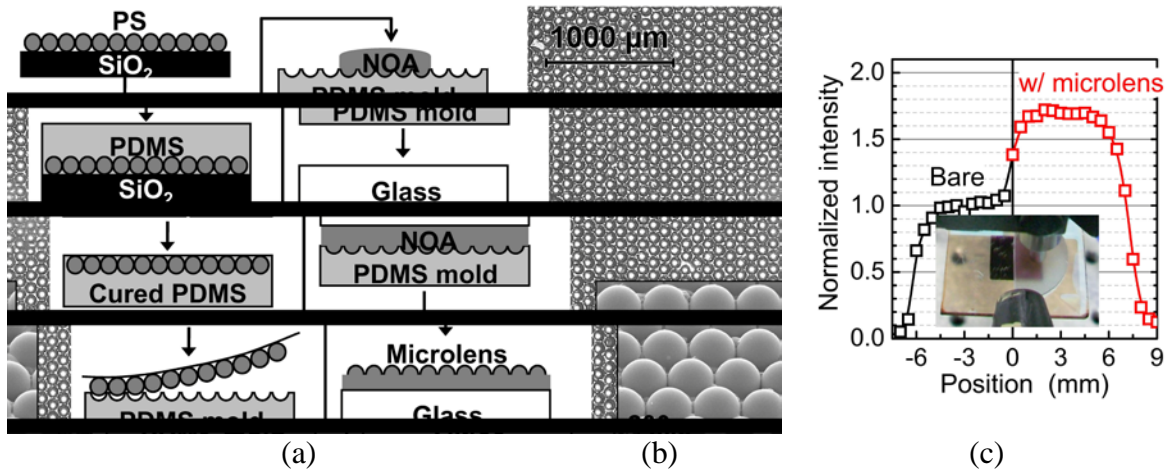


Fig. 7. (a) Schematic illustration of the microlens fabrication process. (b) An optical microscope image of a select area of a microlens array on a 3" wafer. The inset is a SEM image showing the hemispherical shape of the microlenses. (c) Line scan of the normalized emission intensity from a large area OLED where the right half of the device was covered with a microlens array.